

Ab-initio calculations of Many-Body effects in liquids: the electronic excitations of water

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We present *ab-initio* calculations of the excited state properties of liquid water in the framework of Many-Body Green's function formalism. Snapshots taken from molecular dynamics simulations are used as input geometries to calculate electronic and optical spectra, and the results are averaged over the different configurations. The optical absorption spectra with the inclusion of excitonic effects are calculated by solving the Bethe-Salpeter equation. These calculations are made possible by exploiting the insensitivity of screening effects to a particular configuration. The resulting spectra are strongly modified by many-body effects, both concerning peak energies and lineshapes, and are in good agreement with experiments.

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The electronic structure of liquid water is still not fully elucidated, even though it is essential to understand the chemical and physical properties of many biochemical and industrial processes that occur in solution, where it is crucial to include the role of the solvent in the reactions. Water is also essential, both pure and as a solvent, for living organism survival and for biological systems in general. For these reasons the study of the excited state properties of liquid water is fundamental to advance in many research fields. However, in the last years, the theoretical studies of liquid water [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] have mostly focused on its structure and ground state properties whereas less effort has been dedicated to its electronic structure and optical absorption spectrum. As a consequence, experimental data about excited states are poorly understood. One of the purposes of the present work is to solve these issues by carrying out *ab-initio* many-body calculations of the electronic structure and optical spectra of liquid water.

Here we generalize the application of the Many Body Perturbation Theory (MBPT) [11] to liquid systems, and present a calculation of the optical absorption spectrum of liquid water from first principles, including both self-energy effects and the electron-hole interaction. We show the occurrence of important excitonic effects, which are crucial for a good description and interpretation of experimental data.

The main problem concerning the study of liquid water relies on the fact that, in order to simulate a complex disordered system, one should use a very large unit cell, with a consequent prohibitive computational cost. In order to overcome this bottleneck, we used a smaller unit cell but exploiting several molecular dynamics (MD) snapshots of water as input geometries. Averaging

the resulting electronic and optical spectra over many configurations should give a good approximation for the excited states properties of the real system. We used 20 configurations of 17 water molecules in a cubic box with 15 a.u. side and 8 special k-points. This is a quite low number of molecules [10]; still, the computational effort of the many-body calculations for all the configurations would have been almost prohibitive. We will show in the following that one can however restrict the calculation of certain ingredients, in particular of the screening, to a single configuration. In this way the calculations become feasible with a reasonable effort. Already the results obtained for 17 molecules, averaged over several snapshots, well compare with experiments.

The water configurations have been obtained by sampling every 2 ns a 40 ns long classical MD simulation trajectory. A TIP3P water model potential [12] has been used to represent the water molecules in our simulation box. Equations of motion have been integrated numerically using a time-step of 1 fs. The MD run has been done in the NVT ensemble, where thermal equilibrium at 298 K has been achieved applying a Nosé-Hoover thermostat [13]. Despite the small size of our system, the resulting radial distribution functions are in very good agreement with the experimental ones [14], as it is shown in Fig. 1. This confirms that we are using good input geometries for the excited state properties calculations.

We then performed the electronic and spectroscopic calculations on three levels: we started with density functional theory (DFT) [15], [16] to obtain the Kohn-Sham (KS) eigenvalues and eigenvectors. We hence constructed the DFT independent-particle absorption spectrum. As expected, it shows strong discrepancies with

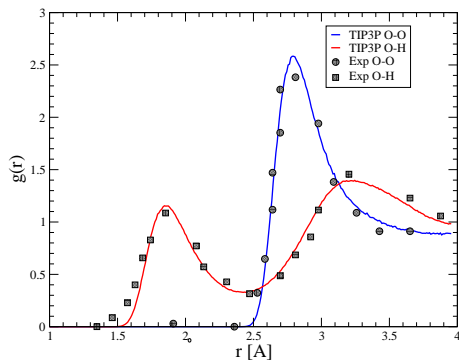


FIG. 1: (Color online) Oxygen-oxygen (blue line) and oxygen-hydrogen (red line) radial distribution functions averaged over the 20 molecular dynamics snapshots compared to experimental data [14] (circles and squares).

respect to experiment. These could not be cured by moving to Time-Dependent (TD) DFT, in the adiabatic LDA (ALDA)[17]. Therefore, we corrected the Kohn-Sham energy levels using the Green's function perturbation approach, with the exchange-correlation self-energy Σ calculated within the GW approximation $\Sigma = iGW$ [18],[11] (G is the one-particle Green's function and $W = \epsilon^{-1}v$ the screened Coulomb interaction). The Quasi-Particle (QP) energies (that is, the electronic 'band structure' of water), were calculated in first order perturbation theory:

$$\epsilon_n^{QP} = \epsilon_n^{DFT} + \Delta\epsilon_n^{QP} = \epsilon_n^{DFT} + \langle n | \Sigma - V_{xc}^{DFT} | n \rangle \quad (1)$$

where V_{xc}^{DFT} is the exchange and correlation KS potential and the self-energy is evaluated at the quasiparticle energy. As a last step, the optical absorption spectrum was calculated by solving the Bethe-Salpeter equation [11], so fully including local-field effects and the electron-hole interaction [19].

DFT-KS results for the electronic and spectroscopic properties of water (obtained averaging over the 8 k points for each of the 20 configurations) are shown in Figs. 2 and 3a. The configuration-averaged HOMO-LUMO gap turned out to be 4.85 eV, in good agreement with previous DFT calculations [1] but strongly underestimating the experimental gap (8.7 ± 0.5 eV [20]), as expected in DFT calculations. Also optical absorption spectra at the DFT independent-particle level obtained for the 20 MD snapshots and, more important, their average (Fig. 3) do not compare in a satisfactory way with the experimental absorption spectrum [21], [22] reported in the inset of Fig.5: we can observe that the onset of the absorption is strongly underestimated in our calculation, the peak positions are red-shifted in comparison to the experiment, and the relative intensities of the first two absorption peaks are not well reproduced.

We have therefore performed calculations of the optical absorption spectrum within TDDFT [17]. In principle this represents an exact way to calculate optical

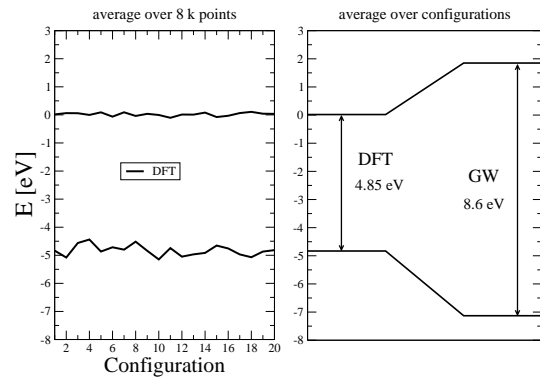


FIG. 2: Left panel: DFT HOMO and LUMO energies, averaged over the 8 k-points, for the 20 MD configurations. Right panel: schematic HOMO-LUMO gaps, calculated within DFT and GW, averaged over the 20 MD configurations.

spectra, but the quality of the results depends on the approximation that is used to describe exchange-correlation effects. A widely used and computationally most efficient approximation is ALDA. Unfortunately our results, shown in Fig. 4a, shows no improvement with respect to the static DFT independent-particle result. Long-range and/or dynamical effects that are missing in the ALDA kernel should hence be important for the absorption spectrum of water, and one has to resort to more elaborate (hence time-consuming) TDDFT approximations [23], or to work in a different framework. We have adopted the latter choice in this work, since Many-Body Perturbation Theory offers a well established way to compute and analyze optical absorption spectra of extended systems.

In order to correct the KS electronic gap and optical spectra, one can calculate the GW corrections $\Delta\epsilon_n^{QP}$ to the KS energies. This should be done for *all* the 20 MD configuration, followed by an average. In particular the calculation of the screened Coulomb interaction for 20 configurations constitutes however a true bottleneck. Instead, one can imagine that a change in configuration does not modify drastically the screening of an additional hole or electron. In fact, changing for example the position in space of an occupied orbital also moves the region of strong screening in the same direction. One can therefore hope that GW corrections $\Delta\epsilon_n^{QP}$ are quite stable with respect to the configuration.

This actually turned out to be true in our calculations. In other words, although the configurations were different, and so were the KS eigenvalues, the difference between DFT and GW, $\Delta GW = \epsilon_n^{QP} - \epsilon_n^{DFT}$, was practically constant going from one snapshot to another. This is shown in table I for three configurations. We could, hence, use the same GW corrections for all the DFT configurations.

The GW corrections increase the electronic HOMO-LUMO gap to 8.6 eV (see Fig. 2) [25], well within the experimental range [20]. (Note that a larger gap, ~ 9.5

	DFTgap	ΔGW HOMO	ΔGW LUMO	ΔGW gap
E19	4.38	-2.02	1.83	3.85
E01	4.72	-2.03	1.82	3.85
E13	4.21	-2.04	1.82	3.86

TABLE I: Test GW corrections to the HOMO and LUMO energy levels and to the electronic gap, for three different water configurations (E19, E01, E13) [24]. Energies in eV.

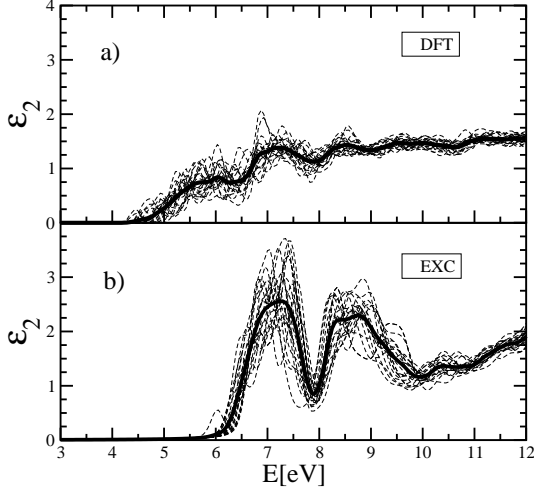


FIG. 3: Optical absorption spectra of the 20 configurations (thin lines) and their average (thick lines). a): DFT single particle calculation; b): with the inclusion of self-energy and electron-hole interaction effects.

eV, is obtained in hexagonal ice [26]. The disordered band-edge landscape leads indeed to a shrinkage of the minimum gap with respect to the reference ordered system, ice in this case.). Since the calculated GW shift is almost constant for all the bands, GW optical spectra show lineshapes very similar to DFT ones, but shifted to higher energies, as shown in Fig. 5. The agreement with the experimental $\epsilon_2(\omega)$ is hence not at all improved, since the relative intensities of the two absorption structures (seen in experiments at 8.3 and 9.6 eV) are still not reproduced, and their position, from being red shifted in DFT calculations (Fig.5, solid line), are now strongly blue shifted in GW (Fig.5, dotted line).

We have hence clear hints that single particle and single quasi-particle approaches are not sufficient to describe the optical properties of water, and that it is necessary to include the electron-hole interaction. To this end we had to solve the Bethe Salpeter equation, where electrons and holes interact through the screened Coulomb potential W . These cumbersome calculations had to be done for all the 20 MD configurations, in order to obtain an average.

Our results are shown in Fig. 3 for all the 20 MD con-

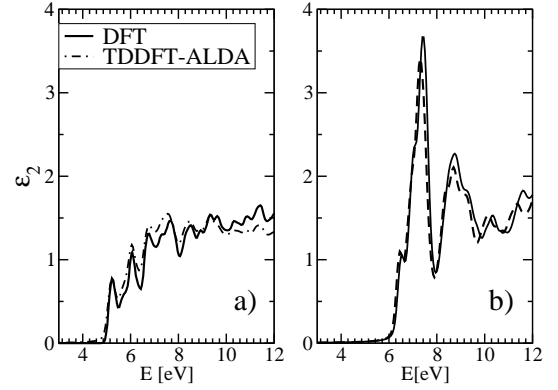


FIG. 4: Optical absorption spectrum for one MD configuration. a) Time Dependent DFT within the Adiabatic LDA vs single particle Kohn-Sham DFT spectrum. b) BSE spectrum calculated using the full screened electron-hole interaction (solid line) and using for W a constant dielectric function $\epsilon^{-1} = 1/1.7$ (dashed line).

figurations and in Fig. 5, where their average is reported (dashed line). Dramatic many-body effects are evident. Agreement with experiment both in energy peak positions and onset, as well as in the relative intensities of the first two peaks, is significantly improved. The main remaining discrepancy is an overall redshift, that might be due to the fact that our GW calculations are not self-consistent but use DFT wavefunctions and energies. The first peak in the spectrum turns out to be a bound exciton with a binding energy of 2.4 eV and large oscillator strength. These are a consequence of the weak electronic dielectric screening of water ($\epsilon_\infty \sim 1.8$). The second peak results from an excitonic enhancement of the oscillator strength of interband transitions with respect to the single quasi-particle case. The binding energy of the lower exciton, although quite large, is smaller than the value $E_b = 3.2$ eV found in hexagonal ice [26]. One can in fact imagine that the mixing of electron-hole pairs of different energy, which leads to the bound exciton, partially counterbalances the disorder effect on the quasiparticle gap [27] (namely the gap shrinking that is determined by a local increase of occupied state energies, and a local decrease of unoccupied state energies). Moreover, the higher density in the liquid phase with respect to ice (around 7%), may also play a role in reducing the exciton binding energy, by allowing a greater mobility of electrons and holes.

It is of fundamental importance to explore also to which extent a detailed calculation of each single configuration is mandatory. In fact, the effect of the electron-hole interaction does not depend significantly on details of the screened Coulomb interaction $W = \epsilon^{-1}v$ [11], but rather on macroscopic averages. Therefore, and as we have explicitly verified, the optical spectra of the various MD configurations can be calculated using for the electron-hole interaction the same screening,

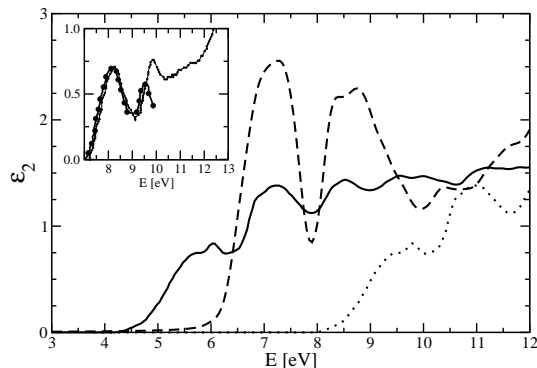


FIG. 5: Calculated optical absorption spectra averaged over 20 configurations. Solid line: single particle DFT spectrum; dotted line: spectrum obtained with the inclusion of the GW corrections; dashed line: spectrum obtained with the inclusion of the electron-hole interaction. Inset: experimental optical absorption spectrum of water (line: [21]; circles: [22]).

$\varepsilon^{-1}(q, \omega)_{G, G'}$, obtained for any of the independent MD snapshots. Moreover, test calculations done using a *constant* value for ε^{-1} have shown that a good agreement can also be obtained using a value for $\varepsilon^{-1} = 1/1.7$, (very near to the experimental macroscopic electronic value $1/1.8$) as shown in Fig.4b.

Our findings concerning the stability of GW and BSE calculations may have important consequences on future calculations for water (and maybe for other liquids), since the *ab-initio* evaluation of $\varepsilon^{-1}(q, \omega)_{G, G'}$ is the real bottleneck of many-body calculations, and its evaluation for many different snapshots makes this approach too cumbersome for becoming a state of the art method. Hence, to be able to determine accurate optical spectra for many configurations, using the same dielectric constant to screen the electron-hole interaction, will enormously speed up the calculations.

In conclusion, we have presented an *ab-initio* many-body calculation of the electronic structure and optical properties of liquid water obtained averaging the results of snapshots taken from molecular dynamics simulation. We have found that the GW corrections are almost independent of the particular snapshot considered and give an average HOMO-LUMO electronic gap of 8.6 eV, smaller than that of hexagonal ice [26], and that the effect of the screened electron-hole interaction is the same for all the configurations. This result implies a huge reduction of the computational effort, and opens a pathway to low cost calculations on other disordered systems.

Absorption spectra calculated with the inclusion of excitonic effects show important structures related to the electron-hole interaction which are essential to obtain a good description of experimental data. The onset position and the relative intensities of the first two peaks

are well reproduced *only if* the electron-hole interaction is fully taken into account. ALDA calculations do not improve at all the DFT spectra.

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- [1] K. Laasonen et al., J. Chem. Phys. **99**, 9080 (1993)
 - [2] O. Christiansen, T. M. Nymand, and K. V. Mikkelsen, J. Chem. Phys. **113**, 8101 (2000)
 - [3] J. C. Grossman et al., J. Chem. Phys. **120**, 300 (2004)
 - [4] M. E. Tuckerman et al., J. Phys. Cond. Matt. **6**, A93 (1994)
 - [5] H. Sato, and F. Hirato, J. Chem. Phys. **111**, 8545 (1999)
 - [6] P. L. Silvestrelli, and M. Parrinello, J. Chem. Phys. **111**, 3572 (1999)
 - [7] B. Chen et al., Phys. Rev. Lett. **91**, 215503 (2003)
 - [8] P. Raitieri, A. Laio, and M. Parrinello, Phys. Rev. Lett. **93**, 087801 (2004)
 - [9] L. Bernasconi et al., J. Chem. Phys. **121**, 11885 (2004)
 - [10] D. Prendergast, J. C. Grossman, and G. Galli, J. Chem. Phys. **123**, 014501 (2005)
 - [11] see e.g. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)
 - [12] W. L. Jorgensen et al., J. Chem. Phys. **79**, 926 (1983)
 - [13] S. J. Nosé, J. Chem. Phys. **81**, 511 (1984); W. G. Hoover, Phys. Rev. **31** A1695 (1985)
 - [14] A. K. Soper, F. Bruni, and M. A. Ricci, J. Chem. Phys. **106**, 247 (1997)
 - [15] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)
 - [16] We perform pseudopotential DFT simulations both in the GGA-PW91 and LDA approximations; although the resulting gaps show differences of about 0.25 eV, the final GW results are independent of the starting point, as expected. We sample the Brillouin zone with a 8 k points mesh and use a kinetic energy cut-off of 50 Ry.
 - [17] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984) ; E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **56**, 2850 (1985)
 - [18] L. Hedin, Phys. Rev. **139**, A796 (1965)
 - [19] Optical absorption spectra at the BSE level have been obtained including all the filled states and 100 empty levels. The resulting 20 excitonic Hamiltonians (one each MD configuration) sized 54400x54400, have been diagonalized using the Haydock algorithm.
 - [20] see e.g. A. Bernas, C. Ferradini, and J. P. Jay-Gerin, Chem. Phys. **222**, 151 (1997) and ref. therein; <http://www.ensta.fr/~muguet/papers/ECCC7/band.html> and ref. therein
 - [21] G. D. Kerr et al., Phys. Rev. A **5**, 2523 (1972)
 - [22] L. R. Painter et al., Phys. Rev. Lett. **21**, 282 (1968)
 - [23] G. Adragna, R. Del Sole and A. Marini, Phys. Rev. B **68**,

- 165108 (2003); F. Sottile, V. Olevano and L. Reining, Phys. Rev. Lett. **91**, 056402 (2003); A. Marini, R. Del Sole and A. Rubio, Phys. Rev. Lett. **91**, 256402 (2003)
- [24] The planewave cutoff energy has been lowered by 40% for these tests. The ΔGW corrections in table I results to be 0.1 eV larger than the well converged values obtained with the higher cutoff.
- [25] GW corrections have been calculated using 19933 plane waves for the exchange part of Σ , and 13997 plane waves for its correlation part. The screened W has been calculated within the plasmon pole model, using 600 empty bands.
- [26] P. H. Hahn et al., Phys. Rev. Lett. **94**, 037404 (2005)
- [27] M.A. Kanehisa, R.J. Elliot, Phys. Rev. **B 35**, 2228 (1987)